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Valorization of Wastes for Biodiesel Production: The Brazilian Case

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Abstract

This chapter intends to bring an overview about the Brazilian researches and their contributions to the production of biodiesel from wastes. Currently, the main obstacles to spread the use of biodiesel are its high cost of production and the competition between biodiesel and food industries. So, the use of wastes plays an important role in reducing the biodiesel costs and reusing the materials that have no other applications, as deodorization residues, neutralization soap sticks, and animal fats, among others. Then, we present a review about Brazilian studies involving waste oils and fatty–acid-rich raw materials that helped the advancement in this field of knowledge during the last few years.

Keywords: waste valorization, Brazil, biofuels, biodiesel

1. Introduction

Since the 1950s, Petroleum has become the most important source of raw material for industrial chemistry and of fuel. Although in recent years, fossil fuel reserves have been provided for the next two decades, particularly heavy oil, tar sands, and deepwater drilling and oil and shale gas have grown, there are large uncertainties in the economy of their exploitation through current methodologies. Therefore, in the future, renewable resources should regain their importance, since the choice of the raw material acquires an ever greater significance, not

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only for economic reasons but also because the initial choice will determine the properties of its derivatives and, consequently, the environmental impacts [1–3].

Non-renewable natural resources, fossil fuels, will not be sustainable in the next century due to the high consumption rate (the rate of global energy use is expected to increase from its current level of about 20–27 TW by 2050 and can reach 43 TW by 2100) [1–3] and the serious environmental problems that accompany their combustion. There is an urgent need to develop new forms of energy that are clean, renewable, and low-cost.

In this sense, several countries have developed treaties proposing a gradual reduction in the use of fossil fuel derivatives, as well as an increase in actions aiming the technological development of biofuel production and consumption, and in this way, to minimize the growing signs of global climate change [4, 5]. Moreover, the interest in the world-wide research in improving the production of better-quality fuels that cause less damage to the environment as well as lower expenses for the producers [6] and Brazil follows the world trends.

Brazil presents a highlighted position about the countries in the world, having 18% of fuel sources and 45% of the energy consumed of renewable while all over the world has 14% of the energy coming from renewable energy sources. In the search for the alternative sources to the use of oil, Brazil presented itself as a pioneer country in the use of biofuels, standing out from many countries that search for sources of renewable energy [7]. For instance, the Brazilian production of alcohol in 2009 reaches 25,866.06 m^3, in contrast to 12,588.00 m^3, before flex-fuel vehicle implantation. For biodiesel, the Brazilian production (**Figure 1**) was 736 m^3 in 2005 to 3,419,838 m^3 in 2014 [8].

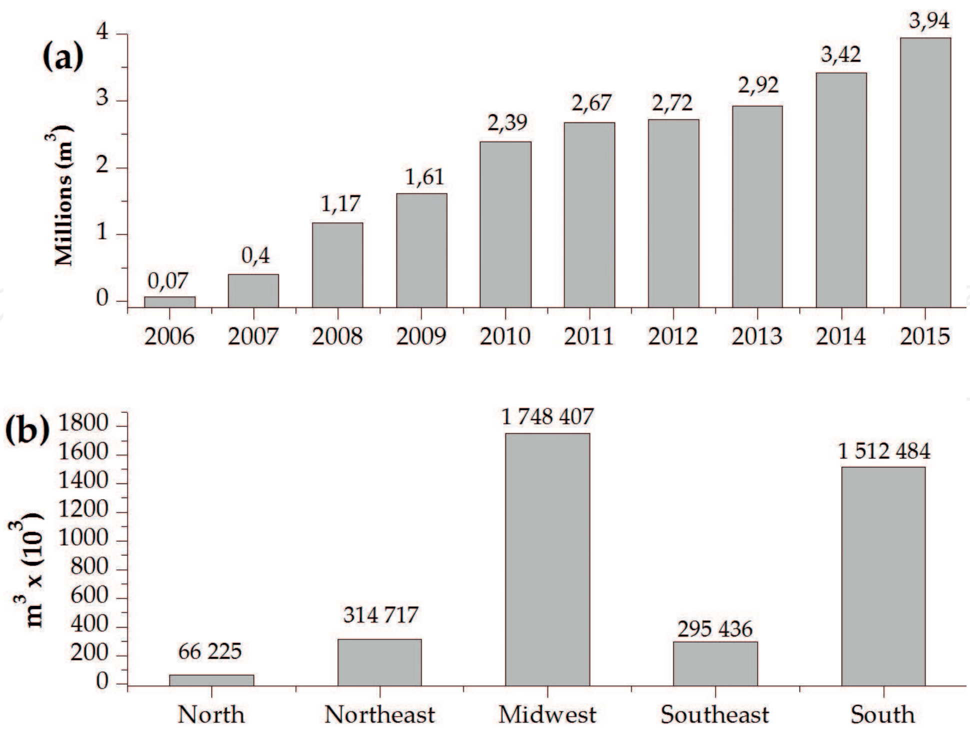

Figure 1. (a) Evolution of biodiesel production; (b) production of biodiesel according to large Brazilian regions in 2015 [4].

This highlighted position can be explained for some reasons. First, Brazil is a tropical country with continental dimensions that allow the exploitation of traditional crops such as sugarcane, soybean, peanut, sunflower, castor bean, and palm oil, as well as new alternatives such as tucumã, babaçu, pequi, buriti, jupati, and a wide variety of oilseeds to be explored. Furthermore, due to its great size and variety of climates with many regions of pastures, it is one of the greatest exporters of bovine meat of the world, which can improve the biodiesel production, as can be seen ahead.

Another reason is its experience to produce biofuels. The first reports of the Brazilian experiments with the production of biodiesel and ethanol are from the 1920s, when the National Institute of Technology began to study these biofuels [9, 10]. However, the high consumption of biofuels in the country occurred in the 1970s, with the implementation of the Brazilian biofuel program PROÁLCOOL (National Alcohol Program). With the experience acquired in the implementation of PROÁLCOOL, the Brazilian government launched in December 2004 the National Program for the Production and Use of Biodiesel (PNPB) [10]. In 2005, it was established by law 11,097 that biodiesel should be blended with petroleum oil in 2% (B2), increasing to 5% (B5) in 2013. Under these conditions, the National Petroleum Agency (ANP) is responsible for regulating and complying with established rules for the commercialization of biofuels, which are currently defined as 8% (B8) of biodiesel in petroleum diesel [7].

Currently, Brazil stands out worldwide for the production of sugarcane alcohol and soybean biodiesel, both considered of first generation. However, their current limitation is their high price, which sometimes approaches the cost of fossil diesel fuel. Therefore, the study of alternative raw materials is of major importance for not competing with the food market and reduces production costs, therefore increasing the economic competitiveness of biofuels [11].

In this way, Brazilian researchers have been studying some alternatives to improve the contribution of these biofuels to the energy matrix. In the case of biodiesel we can cite microalgae [12] and cyanobacteria [13] produced naturally, and some types of non-edible plant oils, such as *Jatropha curcas*, castor bean, Murumuru, buriti, and pracaxi, can play a considerable role in the supply of alternative feedstock. On the other hand, they require a large available farmland [7, 14]. Then, a largely accepted strategy to reduce the cost of biodiesel is the use of wastes for the production of biodiesel; besides bringing substantial environmental benefits, it provides an alternative for the final disposal previously discharged in the environment [7].

Based on this context, this chapter intends to bring a review of researches developed by Brazilian researchers in the field of recovering residues, using different types of approaches related to the subject of Biodiesel.

2. Waste valorization and the biodiesel in Brazil

There is no doubt that the valorization of wastes plays an important role in the field of biofuel generation due to the low price of such feedstocks, which is a fundamental requirement to reduce prices and to increase the competition of biofuels compared to fossil fuels. However, there are several advantages in reusing materials that could damage the environment. It could reduce the pollutant disposal and could possibility increase the employment generation due to the great amount of people that could be involved in the waste recovery and in the biofuel industry. All these findings enforce researchers to evaluate the feedstocks, the best conditions, and the techniques to produce such waste-based biofuels.

From now on, some literature reports (from the last 15 years) will be presented in this point of view. It is important to point out that there are a great number of scientific articles related to this subject using different approaches. From the study of techniques to characterize the different wastes and waste-based biofuels to the study of purification methods of these biofuels, all are reported. Socioeconomic analysis of the waste valorization and the engine tests are also found in the literature.

Despite such diversity, when focusing in waste valorization, it is possible to point out two wastes that have been studied and whose biodiesels have already been produced (even on a microscale): cooking oil and cattle fat. For this reason, both fats will receive a certain highlight in this manuscript. However, other aspects and examples will be mentioned elsewhere.

2.1. Waste cooking oil or frying waste oil (WCO or FWO)

The price of biodiesel is currently the highest selling price since depending on its source it can cost up to 1.5 times more than diesel oil. One way to convey this problem would be the use of oil sources that are the least expensive, such as waste and tailings. The cooking oil used is a raw material that has been used that reduces costs and decreases the amount of material in the environment. In Brazil, the recycling of frying oil is receiving importance and investments from companies interested in carrying out the proper disposal of this waste as well as having an outlook toward profit. Brazil already produces biodiesel from WCO; however, the amount of WCO in the energy matrix is still very low. For instance, just 0.5% of Brazilian biodiesel was produced from WCO in 2015. This value could be very higher, mainly if we consider that Brazil has an estimate of generation of used oils close to 329,020 t/year [7, 15].

Some rural places had problems with de supply of fuel; the WCO would be a good source for biofuels and will solve this problem and besides will change the centralization of the biodiesel production [15].

Some Brazilian researches have been important to increase the knowledge about the WCO biodiesel to improve its role in the energy matrix, as can be seen below:

- In 2000, Costa Neto et al. [16] have presented some comparisons of the quality between the frying oil used as a source of biodiesel and diesel. Were tested your performance in diesel engines even as the characterization of the emissions derived from this process, being observed a significant reduction of fume when biodiesel from waste oil was used. In that year they already alert concerning the importance of a National Program to promote the biodiesel use, which be created just in 2004.
- Hocevar et al. [17] determined the composition in percentage of waste frying oil blends with soy oil, palm oil, and hydrogenated fat by some techniques such as mid-infrared spectroscopy in association with multivariate chemometric analysis. Using this method, a

first estimation of the principal component of oil blends was made possible, as well as the partial least square regression was used to predict the content of each type of oil present in blends of waste frying oil. Then, they showed that this methodology could be very useful for the rapid, reagent-free, low-cost determination of the composition of waste cooking oil and can aid in decision-making regarding the pretreatment of oils and the production routes for biodiesel.

- The current production of biodiesel uses alkaline liquid catalysts that lead to some drawbacks of production like impossibility to reuse the catalyst as well as high corrosiveness of the catalyst. This situation leads to the use of solid catalysts that also show some problems found in the reactive process like the leaching and deactivation of the catalyst in the presence of water during the reaction of esterification of FFA. Considering all this information, in a study of 2011, Silva et al. [18] evaluated the catalytic activity of tin chloride, $SnCl_2$, which is less corrosive, water tolerant, and a recyclable Lewis acid catalyst, in FFA ethanolysis using waste cooking oil samples (WCO) obtaining success reaching high conversions of FFA into FAEE (fatty acid ethyl esters) in almost all catalytic runs; even when compared to pTSA(*p*-toluenesulfonic acid), the SnCl2 catalyst efficiently promoted FFA ethanolysis in the presence of high water concentrations (ca. 5.0% w/w).

- Alberici and co-workers [19] showed that the biodiesel produced from used frying oil show better quality when compared with other common oils. The parameters of quality of biodiesel like the induction period, the acid number, the iodine value, and the heat of combustion were tested in this biofuel. They also reported that an artificial antioxidant, N,N′-di-sec-butyl-p-phenylenediamine, was shown to significantly increase the oxidative stability of the used frying oil biodiesel at a trace level.

- In 2016, Vescovi et al. [20] produced biodiesel from lipase-catalyzed (immobilized *Thermomyces lanuginosus* lipase and immobilized *Candida antarctica* lipase B) hydrolysis of waste cooking oil (WCO) followed by esterification of the hydrolyzed WCO (HWCO). The hydrolysis of acylglycerols was almost complete after 12 h (ca. 94%), and in the esterification step, the conversion was around 90% after 6 h. The purified biodiesel had 91.8 wt% of fatty acid ethyl esters.

- Hydroesterification is innovation biodiesel production using low-cost feedstocks by two steps: hydrolysis of waste cooking oil to FFAs in subcritical water and chemical esterification of FFAs into FAMEs (biodiesel) with methanol. In their paper, Santos and collaborators [21] performed an effective hydrolysis and validated the relationship between FFA and FAME yields; the study with experimental factorial design using a batch reactor with different parameters to obtain an optimal condition for the hydrolysis was used, and they found a conversion of the FFAs into 98.5 wt% of FAMEs with high quality by esterification in biodiesel production, suggesting that the biodiesel produced by the subcritical/chemical hydroesterification process has similar qualities to those of the biodiesel obtained by traditional alkaline transesterification.

- Recently (2018), Poppe et al. [22] described the use of an ultrasound system for the enzymatic transesterification of oils using combi-lipases as a biocatalyst. Reactions were performed in a mixture design of three factors to obtain the ideal mixture of lipases

(CALB, TLL, and RML) according to the composition of fatty acids present in each oil, and the main reaction variables were optimized. After 18 h of reaction, ultrasound provided a biodiesel yield of about 90% when using soybean oil and 70% using the waste oil. They concluded that having a good composition of fatty acids in soybean oil and waste oil the ultrasound technology can increase the yields of the reaction of biodiesel synthesis reaction. Using combi-lipase catalysts and ultrasound, the waste oil can be a good source of biodiesel to decrease the process costs in the enzymatic production of biodiesel.

Moreover, there are in the literature some papers about production of biodiesel on a pilot scale and socioeconomic impacts or life cycle assessment (LCA), as can be seen below:

Schneider et al. [23] aimed to recognize the production condition of waste oils and fats in the urban area of small towns (Arroio do Tigre-State of Rio Grande do Sul-5511 inhabitants) in order to define actions that will reduce the environmental impact of this activity in public places and homes. They analyzed the frying oil from two restaurants and produced biodiesel on a pilot scale with the CH_3ONa catalyst and obtained 96.6% of conversion, and the quality parameters agree with those of the National Petroleum Agency (ANP).

In another paper, Moecke et al. [24] described a biodiesel production plant installed at Pinheira Beach in the state of Santa Catarina (Brazil), and the transesterification production process was used to convert waste cooking oils into biodiesel using basic catalysis in the presence of methanol. A batch system with the capacity to produce 200 L of biodiesel per day was adopted, and a 94.38% ester content was reached. They also discussed the environmental, social, and economic impacts by analyzing the biodiesel production by life cycle assessment (LCA). The LCA shows some categories that most contribute to the emissions in the biodiesel production process. With 92.10% of contribution, the collection stage is the most emitter with a huge difference in the production stages, that they send 7.9% only. This plant of biodiesel production can provide some gains for the local community like the environmental education and cooking oil recycling opportunities.

Recently, Silva Filho and collaborators [25] produced two integrated papers where they first produced biodiesel from waste frying oil and performed a kinetic study of the transesterification reaction for each frying oil source. After that, in a diesel oil engine, they measured energy and greenhouse gas emission efficiency values. Besides that, people answered some questions for the evaluation of the environmental and economic sustainability of the city of São Paulo. Their measurements showed that the biodiesel kinetics were zero order relative to the frying oil concentration, leading to a 90.10% yield, and the biodiesel physicochemical properties agree with the ANP standards. For blends up to 30%, there was a reduction in greenhouse gas emissions by 33% compared to diesel oil. According to the statistical survey, São Paulo has a production potential of more than 8800 m^3/month, which could generate savings of US$ 5,000,000/month or US$ 7,000,000/month considering the sale of excess biodiesel, glycerin, and carbon credits. In this second paper, they related the variation of the concentration of waste frying oil (WFO) with the reaction time and temperature during the transesterification of WFOs collected in São Paulo. Then, the biodiesel samples were mixed with the S-10 diesel oil in order to obtain the B10, B20, B30, B40, B50, B75, and B100 blends, which were tested in a diesel engine, and their power, fuel consumption, and gas emissions (CO, CO_2, and SO_2) have been measured to verify their greenhouse effect and energy efficiency [26].

For the worldwide famous city of Rio de Janeiro, a LCA study was performed by Souza et al. [27]; they analyzed the potential environmental impacts and socioeconomic benefits of installing a pilot plant for biodiesel production from used cooking oil (UCO) collected from hotels, restaurants, and bars in the Copacabana district of Rio de Janeiro, Brazil. An analysis was made of the production of biodiesel by the alkaline transesterification of UCO with ethanol using data taken from a pilot plant with a capacity to produce 250 l/batch. The findings of their economic analysis showed that it would be feasible for the Rio de Janeiro city council to implement a pilot plant in the Copacabana district of the city. The results of the social performance analysis indicated that the project would have a positive impact on local jobs and income generation.

Another study related to ambient aspects was developed in 2017 by D'Agosto et al. [28], in which there is an examination about the CO_2 emissions from the combustion of a biodiesel-diesel blend in stationary internal combustion engines to generate electricity by an original approach. They analyzed emissions according to the feedstock used for biodiesel production—soybean oil, palm oil, waste frying oil—through the methyl and ethyl routes. Besides that, the Tukey test was used, showing that, in general, higher engine loads led to a decrease in CO_2 emissions in comparison with the standard B4 (4% biodiesel) blend mandated in Brazil in that year.

2.2. Animal fats

Most researches related to renewable fuel are mainly focused on obtaining biodiesel obtained from vegetable oils. However, the use of a large supply of vegetable oils as feedstocks may lead to food scarcity because of the edible oil sources, which are primarily meant for human consumption. Consequently, the use of animal fat waste as cheap sources of feedstock in biodiesel production has gained more and more interest, including by Brazilian researchers [29].

2.2.1. Beef tallow

Brazil owns one of the largest cattles in the world, and this helps to explain the fact that, since 2008, the use of beef tallow for biodiesel production has become increasingly significant, accounting for about 20% of sales of this biofuel in the country. [30]. For this reason, a diversity of scientific studies are found in the literature, as described below:

- In a paper of Araújo et al. [31], published in 2010, the transesterification of tallow by homogeneous catalysis with a solution of methanolic KOH was carried out by means of heating and preliminary formation of a microemulsion, and the beef tallow biodiesel was obtained with a high yield (96.26%). The fatty acids from beef tallow were characterized by gas chromatography-mass spectrometry (GC–MS) and quantified by thermogravimetric analysis (TGA). The correlation of data between the TGA and GC-MS techniques showed a good linear correlation coefficient, making it possible and appropriate for employment for compositional studies (%) of saturated and unsaturated fatty acids in samples of biodiesel from beef tallow by thermogravimetric techniques.
- In 2009, Teixeira and co-workers [32] reported that despite the use of ultrasonic energy for biodiesel production from different vegetable oils, its application for biodiesel production

from beef tallow has received little attention. Then, they performed the transesterification of beef tallow with methanol using ultrasound irradiation, and their results indicated that the reaction conversion and biodiesel quality were similar; however, the use of ultrasonic irradiation decreased the reaction time, showing that this method could be a promising alternative to the conventional method.

Considering another energy source, in 2012, Da Rós et al. [33] developed by a full 2^2 factorial design leading to a set of seven runs with different combinations of molar ratio and temperature to find the optimal conditions for the microwave-assisted enzymatic (Burkholderia cepacia immobilized on silica-PVA) synthesis of biodiesel. Their main goal was to reduce the reaction time preliminarily established by a process of conventional heating. Under optimized conditions, almost total fatty acid present in the original beef tallow was converted into ethyl esters, representing an increase in sixfold for the process carried out under conventional heating.

- The nature of the solid residue formed in beef tallow biodiesel from two commercial producers in Brazil was determined by comparative analytical techniques, namely, gas chromatography with flame ionization detector (GC-FID) and thermogravimetry (TG) in a study of Fernandes Júnior and collaborators [34]. Their chromatographic and thermogravimetric results confirmed the nature of the residue as saturated monoglycerides, predominantly monostearin and monopalmitin.

- In another study, Moraes et al. [35] showed that the technique CGxCG can show results of characterization of oils and blends of the biodiesel/petrodiesel providing the percentage of the esters in biodiesel and the diesel blends.

- Even the biodegradation by microbial action was already studied. In their paper, Cazarolli and collaborators [36] compared the microbial growth (spores of the filamentous fungi *Pseudallescheria boydii*) in biodiesel obtained from tallow catalyzed by NaOH or KOH and purified with water or the solid adsorbent magnesium silicate. After 60 days, they related lower biomass formation in the biodiesel NaOH-water followed by biodiesel NaOH-magnesol and that the biodiesel KOH-magnesol and KOH-water favored the biomass formation.

Analogous to the waste oils, the beef tallow has also been studied in terms of its production in pilot scale, blends with diesel, and tests in diesel engines. For instance, Cunha and co-workers [37] produced biodiesel from beef tallow in a pilot plant with the capacity of approximately 800 kg/day. The main conclusion of this work was that the alkaline transesterification of beef tallow with methanol produces a biodiesel with high quality and also with a good conversion ratio, as well as the process is possible but the economical viability must be improved by recovering methanol and glycerol. The obtained results have been used by them for industrial scale-up of the process. Previously, some members of the same research group have been the authors of a study reporting that blends of diesel/biodiesel were produced and assessed in relation to some combustible properties. Their produced blends and biodiesel (B100) were also compared with diesel through consumption tests in a diesel engine used for energy generation, and all tests demonstrated that biodiesel and its formulations with diesel can present similar or better results to those of mineral diesel [38].

In 2011, Corrêa et al. [39] investigated the effect of the blend of biodiesel from beef tallow (B5) in commercial diesel oil on engine performance, analyzing possible internal consequences and characteristics of lubricating oil after the prolonged use in a diesel engine. The engine was operated for 600 hours and its performance was evaluated through tractor power take off (PTO) tests. After the end of the test, the engine performance was satisfactory although there was a tendency of reduction in power and increase in fuel consumption along the 600 hours. In another study with engine tests, Pereira and collaborators [40] realized several tests using beef tallow and beef tallow biodiesel in energy generation. There is also discussion about environmental, social, and economic aspects. Their results for performance and emissions of using beef tallow and beef tallow biodiesel in a stationary engine show, among others, that beef tallow can be successfully applied in compression ignition engine blending with diesel up to 15% of beef tallow. Moreover, the produced biodiesel can be applied in compression ignition engines neatly or blended with diesel in any proportion, with reservations to be used in cold weather conditions when in neat form, due to its relatively low pour point.

In order to obtain a biodiesel with the quality parameters required by the National Petroleum Agency (ANP), several researchers have studied the application and properties of biodiesel blends of beef tallow with biodiesel from other sources. There are also some articles that make a comparative study between biodiesel of animal and vegetable origin.

For instance, Canesin et al. [41] reported that when the parameters of quality of residual bovine and chicken oils were tested, some better points than those of the vegetable oil traditional for the biodiesel production were obtained. While they show a higher concentration of monosaturated and saturated fatty acids with a similar reduction in polyunsaturated fatty acids from soybean, the point of combustion, the flash point, and the density were higher than those of the petroleum diesel. Other parameters were measured like the iodine value that indicates their stability during the storage and showed that the biodiesel from residual oil had satisfactory values that can be improved during the production.

In another study, Teixeira et al. [30] prepared and monitored the quality of blends of beef tallow biodiesel with soybean biodiesel and with conventional mineral diesel fuel to study ideal proportions of the fuels. Measuring the viscosity, density, cold filter plugging point, and flash point (**Table 1**), they demonstrated that tallow biodiesel can be blended with both mineral diesel and soybean biodiesel to improve the characteristics of the blend fuels, over those of the tallow.

Sample	Viscosity at 40°C, $mm^2\ s^{-1}$	Density at 20°C, $kg\ m^{-3}$	Cold filter plugging point, °C	Flash point, °C
Beef tallow biodiesel	4.89	832.0	15	152
Soybean biodiesel	4.20	845.0	4	156
Petrodiesel	3.47	801.4	10	57

Table 1. Results of physicochemical tests performed on beef tallow biodiesel, soybean biodiesel, and petrodiesel samples [32].

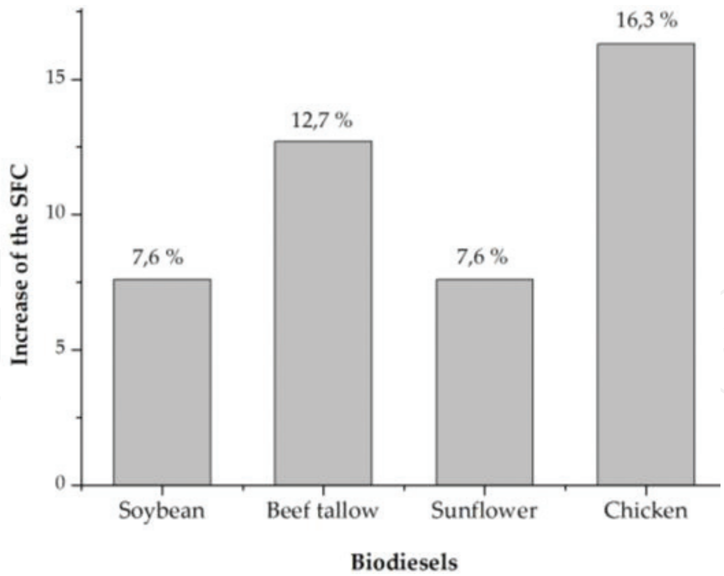

Figure 2. Comparison of the SFC using biodiesels related to the diesel oil [44].

On the other hand, Silva and co-workers [42] evaluated the engine generator (with a power of 7.36 kW on an electric generator with a power of 5.5 kW) performance using biodiesels obtained from soybean, sunflower, chicken fat, and beef tallow and compared them to mineral diesel. When (**Figure 2**) the specific fuel consumption (SFC) and the efficiency (Z) between the diesel oil with the biodiesel from sunflower and soybean oils were compared, biofuels showed a higher performance than the diesel, showing a lower increase of SFC (7.6%) and a slight increase in the overall efficiency.

An interesting approach was made by Pereira et al. [43] who studied an alternative to improve the oxidative quality of vegetable oil biodiesel by blending it with animal fat biodiesel. They studied the oxidative degradation of soybean/beef-tallow biodiesel (SB) 70/30 and 50/50 (w/w) during long-term storage (up to 350 days). The samples were stored and analyzed periodically via oxidative stability, among other analyses and the results showed that the produced blends presented higher oxidative stabilities than soybean biodiesel. During their long-term storage, the biodiesel blends showed greater resistance to oxidative degradation, which was indicated by the lower formation of hydroperoxides and polar compounds. Similarly, the decline in the tocopherol content was slower in SB biodiesel. Then, the prepared blends were appropriate alternatives to improve the oxidative quality of this biofuel. Referring to beef tallow and soybean biodiesel, Soldi et al. [44] synthesized sulfonated polystyrene (SPS) compounds from linear polystyrene (PS), resulting in catalytically active polymeric materials with several sulfonation degrees of dry polymer. The transesterification of beef tallow and soybean oil with ethanol and methanol was used to evaluate their catalytic performance. The SPS samples were insoluble in the reaction media and led to conversions of 85 and 75% of refined soybean oil and beef tallow with a 53 mg KOH/g acid number, respectively. There was an increase in ester production for reactions carried out at a higher methanol:oil molar ratio, and in some cases, products with as much as 94% methyl ester content were obtained, showing that the prepared sulfonated polymeric compounds are efficient catalysts for the these reactions.

Another comparative study was performed by Sales et al. [45], in which ethylic transesterification without any chemical or biochemical catalysts at different subcritical thermodynamic conditions using wet animal fat, soybean oil, and palm oil as feedstocks was realized. Conversions of 100, 84, and 98.5% were obtained for animal fat, soybean oil, and palm oil, respectively. Their results indicate that the process is energetically favorable, representing a cleaner and more advanced technology with environmental advantages for these processes. In another study, Teixeira et al. [46] have determined the physicochemical properties of biodiesel samples produced from mixtures of beef tallow, babassu oil, and soybean oil. The thermo-oxidative stability was evaluated by thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC), and the results showed that the biodiesel obtained from a mixture containing 50% of babassu oil had lower values of pour point, cold filter plugging point, and freezing point.

To finish this sub-section, another comparative paper describes the evaluation of the potential of nonedible feedstocks to yield biodiesel by an enzymatic route (microbial lipase from *Burkholderia cepacia* immobilized on a silica-polyvinyl alcohol matrix). The ethanolysis of native oils from tropical crops, such as andiroba (*Carapa guianensis*), babassu (*Orbignya* sp.), jatropha (*Jatropha curcas*), macaw palm (*Acrocomia aculeata*), palm tree (*Elaeis guineensis*), and beef tallow in a solvent-free system and the biocatalyst were efficient in converting all fatty acids into the corresponding ethyl esters [47].

2.2.2. Other waste animal lipids

Despite the importance of beef tallow, reports about the use of chicken or swine fat, as well as fish oils have also been found in the literature as follows:

- In a study of 2008, Gomes et al. [48] determined certain physical-chemical characteristics of chicken oil that can influence the transesterification reactions of chicken oil. They also evaluated the potential for the production of chicken oil in the cooperatives of the western Paraná State and concluded that with the obtained yield of 95%, it would be possible by these cooperatives to produce up to 74,000 kg of biodiesel.day^{-1}.

- Another study involving chicken was developed by Cunha Jr. et al. [49], in which they optimized the conversion of a mix of chicken and swine fat residues for biodiesel production by a full 3^3 factorial design for process parameters and analyzed their data using response surface methodology. After that, the optimum conditions were applied in a bench-scale reactor and the biofuel produced was characterized (except for oxidative stability and total glycerin, it agreed with quality requirements established by Official Regulations (ASTM 6751 and EN 14214), and it was observed that at high temperatures (50 and 70°C), phase separation between biodiesel and glycerol was impaired. Although high conversion was achieved (96.2%) at 70°C, this condition is not recommended because no spontaneous phase separation was verified. On the other hand, 30°C was the best temperature for biodiesel ethanolysis, with which they achieved around 83% conversion.

An alternative interesting animal source that has been studied by Brazilian researchers to produce biodiesel is the fish oil, once this country possessed large watersheds and an extensive coast. So, following we have some examples of these studies.

Almeida and Spanish collaborators [50] studied the influence of waste fish oil, palm oil, and waste frying oil as raw materials on biodiesel properties. They obtained biodiesel samples with yield higher than 82%, reaching 90% for palm oil (33.3 wt.%) and waste frying oil (66.7 wt.%) biodiesel. The FAME content was higher than 92.3% and had a maximum of 98.5% for waste fish oil (33.3 wt.%) and palm oil (66.7 wt.%) biodiesel. Their multi-objective optimization evidenced that although the use of the pure oils as feedstocks presented more advantages to biodiesel properties, the waste fish oil (42.1 wt.%) and waste frying oil (57.9 wt.%) mix is beneficial.

On the other hand, Mothé et al. [51] determined the optimal reaction conditions for transesterification of waste frying oil and fish by varying the reaction time, amount of catalyst, and temperature and have determined which of these variables exert a greater influence on the reaction yield. So, they found that the amount of catalyst was this variable for the transesterification of waste of the fish oil. So, the produced biodiesel was characterized using thermal analysis techniques and FTIR. The thermogravimetric technique was shown to be an important tool for calculating the yield of transesterification reactions, showing that the majority of TG reactions showed a yield exceeding 90%, a promising result while the FTIR spectra of biofuels obtained from frying and fish oils showed the characteristic regions of esters.

Among several fish species available in the market, the Nile Tilapia (*Oreochromis niloticus*) has an important role as a model of study probably due its rapid growth in fish farms and resistance to poor water quality and diseases, as can be seen in some studies, such as that realized by Santos et al. [52]. In that study, they evaluated the production of methyl esters from (Nile tilapia) oil and methanol using low-frequency high-intensity ultrasound (40 kHz) and response surface methodology (RSM) Their results showed that the most important operating condition affecting the reaction was the alcohol to FFA molar ratio, and it was possible to get a maximum yield of 98.2% after 90 min of reaction.

Another study involving Tilapias oil was performed by Martins and collaborators [53], which assessed mandatory parameters regulated by the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP) for biodiesel from residual tilapia oil. Then, they determined the values of specific mass, kinematic viscosity, water content, acidity level, flash point, and oxidative stability and the calorific value of fish oil biodiesel. Analysis of the biodiesel calorific value reported levels that are similar to those of diesel and indicated that fish oil is a promising alternative for biodiesel manufacturing. The same research group related in another work the evaluation of the yield and acid number of tilapia oil according to the type of waste used as well as the estimation of its potential for biodiesel production as a function of the oil obtained. They concluded that fish oil has potential (up to 370 L of biodiesel per ton of waste processed) to convert waste into biodiesel [54].

About the fish viscera oil, Rodrigues and co-workers [55] reported a study that describes the determination of kinetic and thermodynamic parameters of the degradation process of the biodiesel from this raw material. They performed several analyses of accelerated oxidation of biodiesel (EN 14112) and considered the reaction to be of the first order. Their results showed that the biodiesel oxidation reaction is non-spontaneous ($\Delta G^{\neq} > 0$) and endothermic ($\Delta H^{\neq} > 0$), and that the temperature and the oxidation concentration influence significantly the degradation process of methyl esters.

2.3. Different waste raw materials or applications of waste valorization for biodiesel production

There are other interesting wastes that have been studied for biodiesel production; among them, it is possible to highlight the soap stocks and waste refining oils, as can be seen in some papers, as follows. Soares et al. [56] investigated a new hydroesterification strategy for the production of biodiesel from soybean soap stock acid oil: complete hydrolysis in subcritical water, followed by the use of a packed-bed reactor, containing a fermented solid (Burkholderia cepacia LTEB11) with lipase activity, to obtain and convert the fatty acids to their ethyl esters. When the packed-bed reactor was reused in successive 48-h esterification reactions, they obtained conversions of over 84% of the fatty acids to esters.

Reis and co-workers [57] used three different high-acid-content soapstocks (soybean, palm, and coconut) to be esterified with short-chain alcohols in the presence of Amberlyst-35 (A35) sulfonic resin as a heterogeneous acid catalyst and p-toluenesulfonic acid as a homogeneous catalyst for comparison. Then, they noted that an increase in the hydrocarbon chain decreased the rate of conversion and the microwave irradiation reduced the reaction time from 6 to 1 h and achieved a maximum biodiesel production from coconut and soybean soap stocks and methanol (96–98%). Aguiar and collaborators [58] also used A35 to evaluate and to be compared to Amberlyst-36 and a new sulfonic resin, poly(divinylbenzene), synthesized by them in the laboratory (A-36) as to the catalytic activity for esterification of residue of the palm oil and soybean oil refining industry to produce biodiesel. In that paper, the resin A-36 exhibited catalytic activity similar to that of commercial resin A-35; the best results (87 and 94% for oleic and palmitic acid conversion) were achieved with the new sulfonic resin. When applied for the residue of the palm and soybean oil refining industry, all catalysts showed good conversions (76 and 93%) for all catalysts studied. This was the first example of using DVB sulfonic resins as catalysts in the esterification of fatty acid residues of the palm and soybean oil refining industry.

When palm oil is refined, it generates a residue that corresponds to 4% of the product process called the distillate of deodorization of palm oil (DDOP). The composition of the waste produced in free fatty acids (83%) ensures that they are a good feedstock for biodiesel synthesis [59]. In a study of Nascimento et al. [11], they used a catalyst prepared from a waste material (Amazon flint kaolin) for the esterification of DDPO with methanol, obtaining a maximum esterification activity of 92.8%, affirming that DDPO using that catalyst could be a cheaper alternative for production of biofuels. In sequence, the same research group reported a study where Pires et al. [60] incorporated 12-tungstophosphoric acid (HPW) into kaolin waste (MK700), MCM- 41, MCM-48, and SBA-15, and these obtained solid acid catalysts were used in the esterification reaction of DDPO with ethanol. Their results indicated that HPW supported on kaolin waste (as well as in MCM-41, MCM-48, and SBA-15) that was reaching 83% conversion at 2 h reaction with a 1:10 (DDPO:ethanol) molar ratio can provide significant advances in the development of environmentally benign processes in the biodiesel production.

Another residue was studied by Oliveira et al. [61]. They reported the esterification using waste oil generated in the refining of coconut oil with ethanol and methanol, performing it with and without adsorption of water in order to verify the effect of removing water on the reaction conversion, and conversions of over 99% were observed. Some reactions of synthesis of biodiesel require a huge quantity of álcool for a high yield. An experiment performed with an excess of 200% of álcool in a reaction using a zeolite 3A like adsorbent showed higher yield than the reaction with 800% of excess álcool in a reaction without water adsorption, proving to be a good candidate to be used in the biodiesel industry.

About the use of wastes for biodiesel production, there are still some different reports in the literature; for example, there is one paper that investigated the potential that the yeast *Candida lipolytica* UCP0988, in an anamorphous state, has to produce simultaneously a bioemulsifier and to accumulate lipids using inexpensive and alternative substrates such as waste soybean oil, and one of the biomass obtained was able to accumulate lipids of 0.425 g/g biomass (corresponding to 42.5%), which consisted of palmitic acid (28.4%), stearic acid (7.7%), oleic acid (42.8%), linoleic acid (19.0%), and linolenic acid (2.1%) [62]. In another interesting study, Jesus et al. [63] showed the use of vegetable waste as a potential source of raw material for biofuel production. In the work, the microalga *Chlorella vulgaris* was used to maximize the production of lipids and carbohydrates, and the culture medium was prepared with vegetable waste (pumpkin, zucchini, potato, eggplant, broccoli, carrot, cabbage, tomato, and green bean.) The positive results of this work motivate us to replace traditional culture media with media prepared with vegetable waste.

At last, Gomes & Pasquini [64] described the purification of sunflower-oil-derived biodiesel by dry cold washing using chicken's eggshells (*Gallus Gallus domesticus*), as well as a subsequent comparison with conventional wet washing with hot water and the reuse of eggshells. Both purification methods were efficient in the removal of free glycerin, free fatty acid molecules, and the catalyst. Thus, they provide the advantage of reducing effluent emission as well as offering an application for eggshells of which large amounts are generated due to excessive egg consumption and for which an appropriate use has not yet been found.

3. Conclusions

In this chapter, it was possible to understand the importance of waste valorization for the future of biodiesel production, either by using waste cooking oils and beef tallow or by investigating new techniques for analysis and catalysts and methods of synthesis or by the development of pilot plants and economic studies. If these materials cannot replace totally edible oils or diesel, it is clear that their use could be very higher in the energy matrix. For this reason, all researches have great importance, since those that could help to improve the social inclusion and minimize poverty, even those in which there is an improvement of the biodiesel production, by their properties, yields, process, as well as the production of catalysts more efficient, environmental friendly, among others technical aspects. Considering the highlighted position of Brazil in the world scenario of biofuels (despite the scarcity of research funds in this country), it is also possible to affirm that these researches gave/give a fundamental contribution to this reality, improving methodologies, investigating new types of wastes, upgrading their chain of collect and valorization by sensitizing and including more and more people. At the end, it is possible to conclude that the researched ones developed in Brazil occupy a position of vanguard in the world scene of the researches that involve the use of wastes for the production of biofuels.

Conflict of interest

The authors declare no conflict of interest.

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